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PATENT SPECIFICATION

DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Methods and Composition for the Purification of Gases

- I, ALLEN GARLAND EICKMEYER, citizen of the United States of America, residing at 7204 Cherokee Drive, Prairie Village, Kansas, United States of America, do hereby declare the invention for which I pray that a patent may be granted to me, and the method by which it is to be performed to be particularly described in and by the following statement:—
- This invention relates to improved compositions and processes for selectively removing the acid gases, CO₂ and H₂S, from gas mixtures containing them. The invention is concerned with catalysts for increasing the rate of reaction of aqueous potassium carbonate or borate solutions in absorption and desorption of acid gases and a method of securing good purification with low steam consumption.
- It has been known to treat gas mixtures with aqueous solutions of potassium carbonate for the separation of acid gases, CO₂ and H₂S, in the purification of natural gas and hydrogen used for making ammonia. A solution containing 15% to 40% potassium carbonate contacts the mixed gas in an absorber tower equipped with bubble trays or packing and the acid gases are absorbed in the solution. The solution then enters a regenerator tower, in which the acid gases are removed from the solution by steam stripping. The regenerated solution is continuously recycled to the adsorber. Normally in present conventional methods the absorption is performed under pressure using a hot solution, with little or no cooling after regeneration.
- The hot potassium carbonate process does not require solution heat exchangers and coolers used with the familiar amine scrubbing process. However, in commercial practice, objections have been found to hot carbonate scrubbing. Carbon dioxide is absorbed and desorbed very slowly. This limits both plant capacity and purity of the scrubbed gas. When purifying hydrogen which also contains carbon monoxide (CO), a side reaction occurs
- resulting in an accumulation of potassium formate contamination, which reduces the capacity and depresses the activity of the solution for absorbing CO₂. Similarly, undesirable side reactions have occurred with traces of oxygen and H₂S resulting in potassium sulfate contamination. Such contaminated solution have been treated, purged or discarded. Another objection is that a hot gas-steam mixture leaves the absorber and a cooler-condenser-separator must be provided in the system before further processing or compressing of the scrubbed gas can be practically accomplished. In scrubbing natural gas containing both CO₂ and H₂S, the degree of removal of H₂S is unsatisfactory for pipeline requirements and a subsequent purification system is needed. Regeneration of the solution is incomplete and potassium sulfide accumulates in the circulating solution. It is common practice to follow a hot potassium bulk removal system with amine scrubbing for better purification.
- Some inorganic additives, such as arsenious anhydride (As₂O₃) and selenous and tellurous acid, proposed as solution activators, are not favored because of toxicity and undesirable side reactions. A number of organic additives proposed, such as protides and amino acids, have proved to be unstable under the process conditions.
- Conventional amine systems frequently suffer from corrosion especially in removing high concentrations of CO₂ under pressure. Especially when saturated with CO₂ at high partial pressures, the usual 10%—30% ethanolamine solutions undergo degrading side reactions with CO₂, thereby losing capacity to absorb acidic gases and resulting in corrosive products, which are removed from the system by a purification kettle where the volatile ethanolamine is recovered by distillation. The use of sodium vanadate, which has been proposed as a corrosion inhibitor for amine systems, is usually impractical because, being

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nonvolatile, it is soon removed from the system by the purifier.

My preferred method for securing a high degree of purification of gas mixtures containing acid gases is shown in the accompanying drawing. The drawing shows one embodiment of the method which includes an absorber 1 and a regenerator 2. There are two absorption zones 3 and 4, equipped with packing or bubble trays; also there are two regeneration zones 5 and 6. The crude gas, containing the acid gases, CO_2 and/or H_2S , to be removed, enters the absorber through line 7 and first contacts the hot potassium solution, which is preferably activated by my catalyst composition. In absorption zone 3 the acid gases are removed down to a level ordinarily between 1 and 4% in the gas mixture passing through the chimney tray 8 and entering the second absorption zone 4. After contacting with a lean aqueous monoethanolamine (MEA) solution the purified gas leaving through line 9 ordinarily contains about one part per million of H_2S , if present, and from ten to several hundred PPM of CO_2 depending upon the size of the absorber and regenerator towers.

Tracing the solution circuits, the lean aqueous potassium carbonate solution is sent by pump 10 through line 11 to a midpoint of the absorber 1 below the chimney tray 8. Rich aqueous potassium carbonate solution leaving the absorber through line 12 passes through valve 13 and enters the top of the regenerator 2 passing down over the desorption or regeneration zone 6 wherein acid gases are stripped from the solution by direct contact with a rising current of steam and acid gas, which has passed through the chimney tray 14. The semi-lean potassium carbonate solution accumulating on chimney tray 14 is withdrawn through line 15 and recirculated by pump 10.

Referring to the second solution circuit, lean MEA solution is sent by pump 16 through the cooler 17 and through line 18 to the top of the absorber 1 where it passes down through absorption zone 4, wherein the up-rising gas is finally purified. The rich MEA solution collecting on chimney tray 8 is withdrawn through line 19 and passes through solution heat exchanger 20 (which is not required in some cases), let down valve 21 and line 22 which admits it to a midpoint of the regenerator 2. The solution is regenerated in zone 5 by open steam and/or by steam formed by boiling the amine solution in reboiler 23 which is heated by any suitable medium, such as low pressure steam. Lean MEA solution leaves the bottom of the regenerator through line 24 and passes through the solution heat exchanger 20 and is recirculated by pump 16.

A mixture of steam and acid gas leaves the top of the regenerator through line 25 and passes through cooler condenser 26 wherein the steam is condensed and accumulated in

sump 27. Since MEA is somewhat volatile, the condensate contains a small amount of MEA and it is returned by condensate pump 28 through line 29 to a midpoint of the regenerator below chimney tray 14 or any other suitable point in the amine circuit such as the reboiler 23. Also a small amount of MEA, absorbed by the potassium solution, serves to catalyze this solution. The acid gases CO_2 and/or H_2S leaving the condenser through line 30 may be processed further into urea, dry ice or elemental sulfur.

The potassium carbonate solution charged or supplied as make-up to the system is introduced through pipe 31 into line 15. The charge and make-up amine solution is introduced through pipe 32 to the line connected to the suction of pump 16. If the absorbent solution used is a mixture of potassium carbonate and an amine catalyst, it likewise is introduced through pipe 31.

In the amine circuit, ordinarily an aqueous amine solution would be used but, in the event that simultaneous dehydration of the purified gas is desired, the familiar glycol-amine solution would be employed.

In the case of removing CO_2 from hydrogen in a plant employing two stages of shift conversion of carbon monoxide to carbon dioxide, the absorption zones 3 and 4 would be placed in separate absorbers which would follow the first stage and second stage shift converters, respectively.

I have found that solutions having a low heat of absorption of CO_2 and H_2S , such as potassium salt solution, are well suited to the bulk removal of these acid gases when absorption takes place under pressure. A large amount of solution is required to be circulated but relatively little steam stripping is required for regeneration. On the other hand the solution of an amine, such as monoethanolamine, having a high heat of reaction with CO_2 , is well suited to obtaining a high degree of purification of the scrubbed gas by contact with a low partial pressure of the acid gases. Amine solutions require relatively large amounts of heat for regeneration but since I use a relatively low circulation rate, I find that the heat requirement for regenerating the two different solutions are well matched and that the same stripping steam can be used for the regeneration of both solutions. In this way I can eliminate the need for reboiling the potassium salt solution, which is recirculated to the absorber at the temperature of partial regeneration, which is below the solution boiling point by virtue of being contacted by a mixture of steam and acid gas. This has the advantage of suppressing undesired side reactions as described below. Also I eliminate a second overhead condensing and condensate return system. Furthermore, between the hot and cold absorption zones, I eliminate the familiar gas cooler and, consequently, either

eliminate or reduce the duty and size of the solution heat exchanger. Moreover, I avoid the amine-consuming side reactions and corrosive solution by avoiding contact of the amine solution with CO_2 at high partial pressure.

I have found that the rate of absorption of CO_2 in aqueous solutions of potassium carbonate or potassium borate, or mixtures thereof, is catalyzed by ethylene polyamines, alkenolamines or alkanolamine borates or mixtures of any of these.

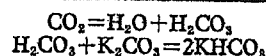
Examples are ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, monoethanolamine, diethanolamine, triethanolamine, dihydroxyethyl ethylenediamine, trihydroxyethyl ethylenediamine, and trihydroxyethyl diethylenetriamine. When negligible vapor pressure is desired in a hot absorption system, polyhydroxyethylamines, such as the last five amines named above, are preferred. I may regenerate solutions, catalyzed by these amines, by means of open steam or gas stripping instead of reboiling. I have found that many other ethylene polyamines and alkanolamines and alkanolamine borates function as catalysts for potassium carbonate or borate solutions, but the above compounds are preferred because of cost.

I have found that CO_2 absorbs at the same slow rate in potassium borate as in potassium carbonate. Therefore, I was surprised to find a very strong catalytic effect on carbonate solutions resulting from the addition of one or more of the above compounds. The chemical structure of the reaction product is uncertain. Boric acid may react with hydroxy groups to give an ester, or with amino groups to give an amine borate, or both reactions may occur. Herein, these products are called "amine borates".

Solutions of amines and amine borates are known alkaline absorbents for CO_2 . However, my experiments showed that small amounts of amines and amine borates are more effective as catalysts in potassium solutions. With an amine borate supplying only 10% of the total alkalinity of my catalyzed potassium carbonate or borate solution, CO_2 is absorbed rapidly, not only at the start but through the entire range of capacity until the solution becomes saturated with CO_2 . Also, throughout regeneration, desorption is rapid.

Potassium carbonate, potassium borate and their mixtures are used preferred as the primary alkaline component of my catalyzed solutions. Catalyzed solutions of sodium salts are not equivalent to potassium in CO_2 absorption rate nor capacity.

It is known that, upon absorption, CO_2 reacts with water and converts potassium carbonate to potassium bicarbonate in accordance with the following reactions:



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The rate limiting step is the hydration of CO_2 and the catalyst facilitates this reaction. An amine borate used alone has some capacity to absorb CO_2 . However, tests with catalyzed potassium solution have proved that the absorption is not preferential; instead the absorption is catalyzed throughout the entire conversion range of potassium carbonate. Thus the mechanism appears to be one of transfer catalysis on the part of CO_2 , or water, or both.

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The preferred composition of my catalyzed solution is dependent upon the composition of the gas to be treated, the gas purity desired, and the temperature and pressure of absorption. The solubility of potassium bicarbonate and/or borate places a practical limit on the maximum potassium solution strength. In general, I start with at least 10% by weight of potassium carbonate or potassium metaborate (or mixtures), in aqueous solution, and I prefer to use between 15 and 40 percent of the potassium compound. Because of the variation of equivalent weight of amines, it is convenient to speak in terms of atomic ratios of amino nitrogen, potassium and boron. On this basis, I prefer to use potassium to amine ratios within the range of 100:1 and 2:1, although I may use higher or lower ratios provided that the potassium salt or salts comprises the major proportion by weight. When CO_2 is the only acid gas to be absorbed, I prefer to use boron to amine ratios of between 1:1 to 2:1, although higher ratios may be used. When H_2S is to be removed, I prefer to increase the proportion of boron or to start with potassium metaborate. I find thereby great improvement in the elimination of H_2S from the regenerated solution and from the treated gas.

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In some cases, for example in removing H_2S and CO_2 from sour natural gas, I use a solution with little amine and a boron to potassium ratio between 0.4:1 and 1.4:1, preferably 0.7—1.1:1. The boron may be added as any of the potassium borate salts. With this solution, I find that the absorption rate of CO_2 relative to H_2S is much reduced. By adjusting the scrubbing solution composition and temperature, practically complete removal of H_2S is obtained while maintaining 1% or 2% CO_2 in the scrubbed gas, which is permitted by pipeline specifications.

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In order to determine the catalytic effect of the compositions of my invention, the reaction kinetics of CO_2 absorption was measured with various solutions under identical conditions of atmospheric pressure and temperatures of 56° C. and 80° C. according to the following tables. Amine borates contribute to the alkali-

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- 5 nity as well as potassium, and the total alkalinity was held constant at about 2.5 normal for the runs in Table 1 and about 4.5 normal for the runs in Tables 2 and 3. At each value for total alkalinity, the relative CO₂ absorption rates are shown with respect to plain potassium carbonate. Since 15% K₂CO₃ absorbed at a faster rate than 25% K₂CO₃, (each without additives), the relative CO₂ absorption rates of Table 1 are not directly comparable with those of Tables 2 and 3. In order to distinguish readily between runs of different total alkalinity, in the
- 15 atomic B:K:N ratios, potassium (or sodium —shown for comparative purposes) was arbitrarily assigned a value of 6 for 2.5 normal solutions and 10 for 4.5 normal solutions.
- 20 The data of Table 1 shows that my catalyzed solutions of preferred compositions absorb CO₂ more rapidly than a solution of any component alone. Compared with dilute solutions, I found that solutions of higher concentration, having less water, absorb CO₂ more slowly. Therefore, they respond more dramatically to catalysts, as shown by a comparison of Table 2
- 25 with Table 1.

TABLE 1

Runs with 2.5 normal total alkalinity:

B:K:N Ratio	Amine Reacted	Relative CO ₂ Absorption Rate
0:6:0 (15% K ₂ CO ₃)	None	1.0
6:6:0 (KBO ₃)	None	1.2
6:0:6 (DEA Meta borate)	DEA	2.8
0.5:6:0.25	DEA	2.4
1:6:0.5	DEA	3.2
2:6:1	DEA	4.1
1:6:1	DEA	3.8
3:6:3	DEA	4.0
6:6:3	DEA	3.3
3:6:1	DEA	3.5
2:6:1	MEA	3.5
2:6:1	TEA	1.9
1:6:1	EDA	2.8
2:6:1	TETA—EO	4.4
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B:Na:N Ratio		
1:6:1 (Starting with Na ₂ CO ₃)	DEA	2.2

Note: DEA is diethanolamine, MEA is monoethanolamine, TEA is triethanolamine, EDA is ethylenediamine, and TETA—EO is the reaction product of triethylenetetramine and ethylene oxide.

TABLE 2

Runs with 4.5 normal total alkalinity:

B:K:N Ratio	Amine Reacted	Relative CO ₂ Absorption Rate
0:10:0 (25% K ₂ CO ₃)	None	1.0
1:10:1	DEA	4.3
2:10:2	DEA	6.9

TABLE 3

Runs starting with 4.5 normal solution from an operating hot carbonate plant. (Solution was cloudy and contained dissolved and suspended foreign material):

B:K:N Ratio	Amine Reacted	Relative CO ₂ Absorption Rate Compared with 25% K ₂ CO ₃ in Table II
0:10:0 (25% K ₂ CO ₃ solution)	None	0.7
1:10:1	DEA	3.1
2:10:2	DEA	4.9
4:10:2	DEA	4.5

My catalysts permit the use of solutions of higher strength and acid gas capacity than solutions now commonly employed in hot carbonate systems. This, and more complete regeneration, results in a substantial reduction in solution circulation rate, increased capacity of an existing plant or smaller equipment for a new plant, reduction in heat for regeneration, and improved gas purification. In many cases, the improved purification eliminates the need for a second scrubbing system, such as the familiar monoethanolamine scrubbing following hot carbonate scrubbing.

My catalyzed solutions are characterized by the low heat of absorption of a potassium carbonate solution and the high activity of an amine solution without the familiar disadvantages of concentrated amine solutions, which suffer from side reactions and corrosiveness and require continual purification by distillation. By much testing I have found that corrosion of carbon steel by my catalyzed solutions can be inhibited by 1000—2000 PPM, or more or less (as V₂O₅ equivalent), of an alkali metal vanadate, vanadite or arsenite, with insignificant losses of inhibitor.

My preferred catalyzed solutions include a small amount of potassium vanadite or vanadate except when the gas being scrubbed contains sufficient H₂S, relative to CO₂, to inhibit corrosion of carbon steel. Also I have found it possible to dissolve 1.0%—2.0% of the vanadium inhibitor, expressed as V₂O₅ equivalent, in a concentrated (50—80%) amine borate solution which may be conveniently added to a potassium salt solution to activate the solution and simultaneously to protect the equipment from corrosion. Potassium dichromate, which is commonly used in hot potassium carbonate systems, is not compatible with my catalyst because of an oxidation-reduction reaction which destroys both the inhibitor and the amine compound.

While my catalyzed solutions improve the degree of purification of the scrubbed gas in systems having a single stage of absorption and regeneration, for those instances where better purification is required, such as 0.03%—0.5% CO₂ or 0—4 PPM H₂S by volume, I use a single solution in a two-stage system. Referring to the drawing and explaining this modified operation, I scrub

the gas with major and minor streams of semi-lean and lean catalyzed solution and may eliminate chimney tray 8, line 19, solution heat exchanger 20, let down valve 21 and line 22. (Solution overflows chimney tray 14 and enters regeneration zone 5). Also, I then prefer to send the condensation in line 29 to the reboiler 23 or, in the case of open steam or gas stripping, I may waste the condensate or send it to a degasifier and then to a steam generator, not shown. I may also eliminate cooler-condenser 26, sump 27, pump 28, and lines 29 and 30; whereupon the mixture of steam and/or gas and acid gas, leaving the top of the regenerator, is sent either to the atmosphere or to further processing, for example, steam-CO₂-methane reforming. Furthermore, I may use a gas, such as methane, nitrogen, air or other gas, for direct contact cooling and/or regenerating the solution in zone 5. The gas may be preheated and/or prehumidified before sending it into zone 5 and open or closed steam may be brought into a midpoint or a point above zone 5, which may have two or more beds of packing.

My catalyzed solution improves the degree of acid gas absorption in zone 3, as compared with an ordinary potassium carbonate solution, so that the lean catalyzed solution can be a much smaller proportion, for example, one tenth, of the total solution circulated; whereas $\frac{1}{4}$ to $\frac{1}{2}$ has been the usual practice. Also, I have found that the high activity of the catalyzed potassium solution made practical the absorption at ambient temperature, which I prefer for the minor stream of solution entering absorption zone 4 through line 18. The solution then cools the purified gas to ambient temperature for compression.

The cooled minor stream also cools the major stream by mixing on a liquid distributor tray (not shown) located at the top of absorption zone 3. In this fashion a most desirable absorption temperature pattern can be obtained, for the purpose of both absorption and suppression of undesired side reactions. It has been determined that the rate of the formate side reaction is much more rapid with a lean solution than with a rich solution and that the rate increases with temperature. Therefore, in practicing the invention, there is no large accumulation of potassium formate, which has troubled ordinary hot carbonate systems.

The scrubbing method is not limited with respect to absorption and regeneration temperatures and pressures except by practical considerations of available materials of construction and their corrosion resisting properties.

EXAMPLES.

In a pilot plant using 15% potassium carbonate with hot absorption of CO₂, the steam consumption for regenerating the solution was

52.6 pounds per hour. It was possible to obtain similar performance with only 34.0 pounds per hour of steam after adding 0.2 pound of tetraethylenepentamine per gallon of solution. In another set of runs when the steam consumption was held constant, the additive caused a 65% increase in the CO₂ carrying capacity of the solution.

Tests of an amine borate catalyst were made with the hot potassium scrubbing system in an ammonia plant in order to determine whether another absorber would be needed upon expanding the plant in the future. In a comparison of special test periods it was found that a 40% increase in CO₂ removal capacity was obtainable while maintaining the same residual CO₂ content of the scrubbed gas simply by adding about 7% of the catalyst to the potassium carbonate solution and increasing the solution circulation 14%. On the basis of these tests the projected installation of another tower was cancelled.

The chemical and thermal stability of the amine borate catalyst was proved by tests of long duration in a similar scrubbing system of another ammonia plant. During the first week after adding catalyst, tests were run under prescribed conditions. During the next four months only nominal losses of the catalyst occurred and these losses were found to be in proportion to the potassium carbonate losses. After seven months of operation under different conditions it was convenient to check the performance of the system under original prescribed conditions. A duplication of the original results proved that there was no significant detrimental change of the solution properties and that the catalyst had remained active. In the meantime it was not necessary to purify the solution in any way.

The shift converter catalyst of this ammonia plant was replaced, after which some H₂S appeared in the gas entering the absorber. The purified gas leaving the absorber contained only 0.1 part per million of H₂S, thus proving the results predicted by laboratory tests.

WHAT I CLAIM IS:—

1. A composition suitable for selectively removing the acid gases CO₂ and/or H₂S from gaseous mixtures containing them comprising an aqueous solution of a major proportion by weight of potassium carbonate or potassium borate or a mixture of both activated by a minor proportion of ethylene polyamines, alkanolamines or alkanolamine borates or mixtures of any of these.

2. A composition as claimed in claim 1 wherein the aqueous solution contains at least 15% by weight of the potassium carbonate or potassium borate.

3. A composition as claimed in claim 1 or claim 2 wherein the atomic ratio of potassium to amino nitrogen in the solution is between 1:1 and 100:1.

4. A composition as claimed in any of the

- above claims wherein the atomic ratio of boron to amine nitrogen in the solution is between 1:1 and 2:1.
- 5 5. A composition as claimed in any of the above claims wherein the atomic ratio of boron to potassium in the solution is between 0.4:1 and 1.4:1.
- 10 6. A composition as claimed in any of the above claims wherein the solution also contains a corrosion inhibitor, preferably a vanadium or arsenic compound.
- 15 7. A composition as claimed in any of the above claims wherein the alkanolamine is the reaction product of ethylene diamine, diethylene triamine triethylene tetraamine or tetra ethylene pentamine and ethylene oxide.
8. A composition as claimed in any of claims 1 to 6 wherein the alkanolamine is monoethanolamine or diethanolamine.
- 20 9. A process for removing CO₂ and/or H₂S from gas mixtures containing one or both of them comprising contacting the gas mixture with a composition as claimed in any of the above claims.
- 25 10. A process as claimed in claim 9 wherein the purified gas mixture is separated from the absorbent solution, the absorbent solution is regenerated in a steam regeneration step and the regenerated absorbent solution is re-used for contacting the gas mixture. 30
11. A process according to claim 9 or claim 10 wherein the absorption of the CO₂ and/or H₂S is conducted in two stages and the regeneration is also conducted in two stages, the partially regenerated absorbent solution from the first regeneration stage being recycled to the first absorption step and the regenerated absorbent solution from the second regeneration stage to the second absorption step. 35 40
12. A process as claimed in claim 11 wherein the temperature of the second absorption stage is less than that of the first absorption stage and the temperature of the first regeneration stage is less than that of the second regeneration stage. 45
13. A process as claimed in claim 11 or claim 12 wherein the regenerated solution for the second regeneration stage is cooled before recycling to the second absorption stage. 50

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